LIME ENHANCED DIRECT REDUCTION OF GALENA BY HYDROGEN

by

DEBAJYOTI BANDYOPADHYAY

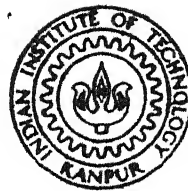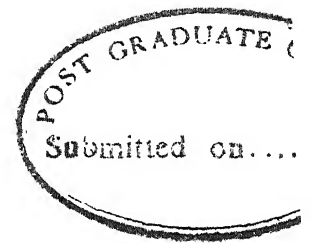DEPARTMENT OF METALLURGICAL ENGINEERING
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A thesis submitted

In Partial Fulfilment of the Requirements

for the degree of

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by

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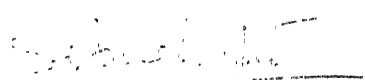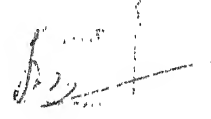
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CERTIFICATE

Certified that this work on '' ~~████████~~ " Lime Enhanced Direct Reduction of Galena by Hydrogen'' has been carried out under my supervision and that it has not been submitted elsewhere for a degree.

Dated: August 1, 1980

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ACKNOWLEDGEMENT

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ABSTRACT

Direct reduction of sulfide minerals by hydrogen
in presence of lime is a probable alternative route for the
extraction of non-ferrous metals. It can substantially reduce
the sulfur pollution problem of the atmosphere due to evolution
of sulfur bearing gases during the unit operations like roasting
smelting etc. in the conventional pyrometallurgical route. A
study of reduction behaviour of galena by hydrogen in presence
of lime has been carried out at temperatures 650°C, 700°C,
750°C, 800°C with hydrogen flow rate of 150 c.c/min and 300 c.c/
Cylindrical pellets of galena, having varying amount of CaO/PbS
ratio (R), namely from 0,1,2,4, and porosity varying from 10% -
16% were used.

Since galena has a high vapor pressure at temperature
examined in this study, its vaporization kinetics also become
important and therefore a study of vaporization kinetics of
galena at temperatures 650°C, 700°C, 750°C, 800°C in nitrogen
atmosphere was also carried out at three different flow rates
of nitrogen, namely 200 c.c./min, 400 c.c./min and 600 c.c min.
The composition and the geometry of the galena samples were
identical to those employed in reduction studies.

Both the evaporation and reduction studies were
carried out using Thermogravimetric Analysis Technique. For
vaporization experiments, it was found that the % wt. loss
vs time plots remained almost linear except for high temperatu

when lime was used . With increase of temperature, nitrogen gas flow rate and lime content, The weight loss due to vaporization also increased. Activation energy for vaporization under various experimental conditions were calculated from rate constant data (k_v) and found to be 30 K- Cal/ mole. It was noticed that the log k_v vs $\frac{1}{T}$ plots remained almost parallel, indicatin that lime did not change the basic mechanism of vaporization.

During reduction, as the total weight loss comprised of weight loss by vaporization plus weight loss due to reducti The weight loss by reduction only was calculated by assuming that the vaporization kinetics of galena in hydrogen to be san as in nitrogen. Weight loss due to reduction was found to be higher with increase of hydrogen flow rate and temperature, ex at higher temperature due to sintering. Predominacy of scavang reaction was established and reduction was enhanced in presenc of lime.

CHAPTER -1

INTRODUCTION

About one third of naturally occurring metal ores are found in form of their sulfide and some of the common metals like Cu, Zn, Pb, Sb, Ni, Mo, Co etc. are produced from their sulfide ores using pyrometallurgical routes. The conventional pyrometallurgical routes of extraction of metals from sulphide ores includes at least two unit operations: (i) roasting and (ii) smelting. In both these unit operations considerable amount of SO_2 and other sulfur bearing gases are produced. Although in many plants a major fraction of these gases are converted into sulfuric acid, outgoing gases still contain substantially high concentration of sulfur bearing gases. Only limited demand of sulfuric acid and the problems associated with the storage of large quantities of acid, makes the storage of sulfur in this form least attractive. Further the multiplicity of unit operations involved in the conventional process complicates the problem of removing the sulfur bearing gases from the flue gas before releasing it into the atmosphere.

Thus, one of the main problems with the conventional pyrometallurgical route of extraction of metals from their sulfide ores is of atmospheric pollution. Continuous liberation of sulfur bearing gases in atmosphere can bring about

pollution beyond tolerable limits. In fact, in many western countries there are very strict city-pollution laws. The pollution problem in the conventional pyrometallurgical route has thus perhaps become the main bottle neck that has forced the extractive metallurgists to think for the alternative processes involving fewer unit operations and in which the amount of sulfur bearing gases produced is drastically cut down.

Years long efforts in this direction have resulted in many newer processes. Some of which have been successfully tried on laboratory scale. One of the processes which has shown great potential is the one based on direct reduction of metal sulphides with hydrogen involving a reaction of the following type.

$$MS + H_2 \longrightarrow M + H_2S \uparrow$$

The H_2S gas, that is produced in this reduction, immediately reacts with some appropriate scavanging compounds to form a solid sulfide. Thus, the outgoing gas contains only a small amount of sulfur bearing gases. Further the process involves only one unit operation, This process has been extensively studied for metals like Cu,Ni,Mo,Zn,Pb,Sb,Co etc.[1-10]

The main objective of the present investigation is to

explore the possibility of using this direct reduction
process for extraction of lead from its sulfide (galena)
concentrate. From the thermodynamic consideration, which
we shall discuss in details in one of the following chapters,
it is obvious that the rate of reduction of sulfide is enhan-
ced in presence of scavenging element/ compound that has a
strong affinity $\underset{\text{with}}{\underline{}}$ sulfur. Thus, the scavanging compound not
only converts the sulfur bearinggases into less harmful form,
but also enhances the rate of reduction. Some of the studies
on direct reduction of sulfides of common metals reported in
literature indicate that lime is one of the very effective
scavanging compounds[20-28] both from economic point of view
as well as its affinity towards sulfur. Thus the kinetic
study of lime enhanced direct reduction of galena with hydro-
gen is the primary interest of this thesis. One major differ-
ence with behaviour of lead sulphide with those of sulfides
of most other common metals is that,lead sulfides has a very
high vapour pressure at temperature normally employed for
reduction,. Therefore, any study on reduction of lead sulfide
would automatically require an extensive study on its vapori-
zation. Hence in the present study also vaporization of lead
under various experimental conditions, employed in the reduc-
tion studies, has been investigated.

This thesis is divided in seven chapters. The second chapter deals with the literature review, the third chapter gives an account of the thermodynamic consideration of scavenged reaction, the fourth chapter contains experimental. Fifth chapter gives the experimental results and discussion of evaporation and reduction study, the sixth chapter takes into account the conclusion and finally the seventh chapter presents the appendix.

CHAPTER -2

LITERATURE REVIEW

Direct reduction of sulfide concentrates with hydrogen, being one of the potential alternative processes for extraction of non-ferrous metals, have been extensively studied. A review of literature on those studies has been made and presented in this chapter.

2.1 Reduction of Copper Sulfide

In 1967 Tanaka et al.[1] were amongst the first investigators to study the reduction kinetics of cuprous sulfide by hydrogen with an objective to replace the preliminary roasting unit operation in the conventional copper extraction extraction process and they were not much concerned about the pollution problem. They calculated the rate of reaction by using Arrhenius Absolute Reaction Rate theory.

Habasi and co-workers [2-5] conducted poineering investigation on the hydrogen reduction of number of sulfides of copper such as Cu_2S, CuS, bornite (Cu_5FeS_4) and Chalcopyrite concentrate in presence of lime and reported that all these sulfides could be successfully desulfurized and that copper could be produced by such a direct reduction process. But inspite of their elaborate experimentation they did not make

any serious attempt to study the effects of various operating parameters that would effect the process kinetics. Mankhand et al.[6] made an elaborate study of the process kinetics and the effect of various parameters with Cu_2S. They showed that the presence of lime, along with H_2 as a reducing agent enhanced the reduction rate to a large extent. Thermodynamic considerations which led to this condusion are summarized in Table 2.1.

From Table 2.1 it is obvious that the values of the equilibrium constants for the reaction (2.3) are about 2-3 orders of magnitude greater than those for reaction (2.1) at various temperatures. Mankhand et al.[6] further observed that the/rate of cuprous sulfide reduction was dependant on various factors like hydrogen flow rate, temperature, particle size, lime content etc. The reduction reaction had higher efficiency at the low gas flow rate. Very high flow rate of hydrogen, reduced the partial pressure of H_2S gas which, in turn, adversely affected the reaction between H_2S and lime. Reduction rate was highly dependent on temperature, low scavanging capacity of lime reduced the reduction rate. Finer particle size of Cu_2S and the lime content greater than the stochiometry (about up to R=3 where R is Amount of CaO/ Amount of Cu_2S) resulted in enhanced reduction kinetics. The reaction of Cu_2S converted to mettalic copper can be estimated either by a chemical

TABLE — 2.1

Thermodynamic consideration of the direct reduction of

cuprous sulfide with hydrogen, with and without lime.

$Cu_2S(s) + H_2(g) \rightleftharpoons 2 Cu(s) + H_2S(g)$ .....(2.1)

	$G^\circ 1000^\circ K$ (k.Cal)	$H^\circ 298^\circ K$ (K.Cal)
	14.3	14.7

$CaO(s) + H_2S(g) \rightleftharpoons CaS(s) + H_2O(g)$ .....(2.2) −15.0   −11.3

$Cu_2S(s) + CaO(s) + H_2(g) \rightleftharpoons Cu(s) + CaS(s) + H_2O(g)$ ..(2.3) −0.7   3.4
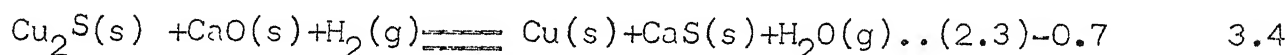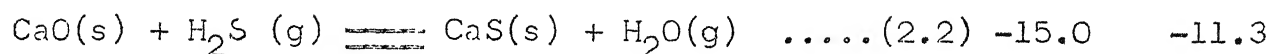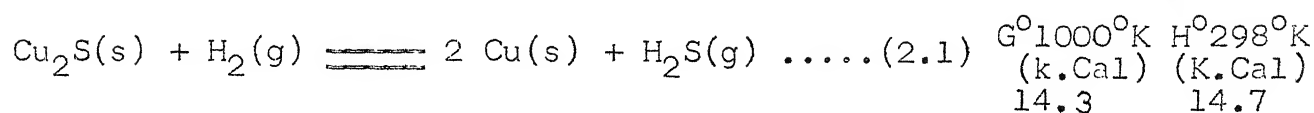
$K_1 = pH_2S/pH_2;$ $K_2 = pH_2O/pH_2S;$ $K_3 = pH_2O/pH_2$

Equation constants for reaction 1,2 and 3

Temperature ($^\circ K$)	K_1	K_2	$K_3 (K_1 \cdot K_2)$
900	4.27×10^{-4}	4.4×10^2	1.88
1000	7.48×10^{-4}	1.85×10^3	1.39
400	1.17×10^{-3}	9.09×10^2	1.06
1200	1.67×10^{-3}	5.06×10^2	0.85
1300	2.25×10^{-3}	3.05×10^2	0.69

From the Table 2.1 it is obvious that the values of the
equilibrium constants for the reaction (2.3) are about 2-3 order
of magnitude greater than those for reaction (2.1) at various
temperatures.

analysis route [11] or by Thermogravimetric Analysis[6] (TGA).

In his study on copper sulfide reduction Cech[12] observed that though the incubation period for reduction was appreciably reduced in presence of lime, the total lime required for reduction was not much affected. At low temperatures, $400^\circ C$, $500^\circ C$ copper grows [12] in the form of occassional fibers whereas at high temperature like $700^\circ C$ it is found in the form of sponge.

2.2 Reduction of Cobalt Sulfide :-

Reduction of cobalt sulfide with hydrogen in presence of lime was carried out by Ford et al[13]. They took into account the benificial effect of lime on the reduction kinetics and found that the increase in lime content increased the reduction rate (e.g. ˉ5 fold increase in conversion at $700^\circ C$ was achieved with lime over the hydrogen reduction without lime). However, over a value of R>3 (R= amount of lime/amount of CoS) lime. acted as an inert filler only. They further reported that at higher temperatures the scavenged reaction becomes slightly sensitive to change in temperature, but this conclusion seems to be erroneous. They also reported that the best scavenging reaction was achieved at low hydrogen flow rate and the reaction was associated with an incubation period. The latter phenomenon is attributed to slow neucleation

process occurring in the metal sulfide. Cobalt sulfide is a metal deficit compound.[14] On exposure to hydrogen atmosphere, sulfur atoms are first removed and thus the metal deficiency decreases. The metal ions diffuse to the bulk of the metal-sulfide which gradually becomes super-saturated with respect to the metal.[15] Accordingly neucleation of metal becomes possible. Once metal nuclei are formed, they start growing on the surface of the sulfide. Cech et al[12] made an attempt to study the morphology of cobalt formation. They found that by using 10 pct. H_2 and 90 pct. N_2 mixture, reduction in the temperature interval of 870^oC to 878^oC produced masses of irregular fibers with some single crystal filaments near the higher temperature. At 879^oC and 880^oC coarse columnar crystals were observed whereas above 880^oC, the reduced cobalt particals were spherical.

A Ni-Co mixed sulfide[12] needed the same highly diluted reducing gas as was used for cobalt sulfide to produce fibrous cobalt in temperature interval of 750^oC to 805^oC. Above 805^oC, only spherical particles were produced. Reduction below 750^oC was very slow with an incubation period of an hour or more.

2.3 Reduction of Molybdenum Sulfide:-

First attempt of direct reduction of molybdenum sulfide (Molybdenite) was made by Key[16] who found that

about 80% desulfurization could be achieved at 980°C.

Mankhand et al [17] in their study on reduction of molybdenite observed that its reduction with hydrogen enhanced substantially in presence of lime and that the scavenged reaction could be carried out almost isothermally.

Percentage desulfurization could be estimated by using the TGA method. Effects of H_2 flow rate, lime and temperature on the reduction kinetics were similar to those reported for other metal sulfides. At higher temperatures (1000°C and above) the reduction rate, however, decreased because of sintering of the sulfide particles.

2.4 Reduction of Nickel Sulfide:-

Cech et al [12] investigated the reduction of nickel sulfide using synthetic sulfide samples. They reported that the reduction to about 80 pct. produced at a nearly constant velocity. Superiority of scavenged reaction by lime over direct reduction and over other scavenging compounds like $CaCO_3$ (before decomposition temperature) was established. It was found that for the reaction without lime, the rate was independent of temperature indicating that the rate was dependent on the rate at which H_2S evolved was transported by the flowing gas.

Reduction experiments carried out near 600°C revealed that the sulfide was reduced to a mass of nickel filaments. In the temperature range between 535°C to 565°C, the fibers were irregular where-as in between 565°C to 590°C, they were a mixture of irregular and straight sided fibers. As the reduction temperature was increased from 590°C to 630°C, fibers became entirely fine and straight-sided. Temperatures between 630°C to 637°C produced numerous short columnar crystals in the filamentary mass where-as at temperature above 638°C, produced only dense spherical particles of metal.

Using the natural nickel sulfide ones· Shah et al.[18] and Byerley et al.[19] examined the possibility of nickel extraction by direct hydrogen reduction of metal sulfide in molten state.

2.5 Reduction of Antimony Sulfide:-

Not much literature is available on reduction of antimony sulfide. Torma et al[29] studied the hydrogen reduction of stibnite both without and with lime and magnesium oxide. They could achieve complete desulfurization in presence of lime or MgO at a temperature of 510°C with hydrogen flow rate of 100 c.c/min within 60 minutes where-as with the same experimental condition but without lime, the yeild was only 54.5% desulfurization.

2.6   Reduction of Lead Sulfide:-

Spagola [30] is among the first investigators to study the direct reduction of PbS and ZnS in solid state. He reported that the solid state reduction was slow and time dependant.   Due to the partial reduction of the outer layers of the charge, the contact between metal sulfide and the reducing gas was interrupted.   The reduction was also damped considerably in presence of gangue material.

The possibility of volatilizing certain metal sulfides has been considered by several investigators. Hsiao and Schlechten [31] measured the vapour pressure of a number of metal sulfide by measuring the rate of weight loss under vacuum. On the basis of vaporization kinetics experiments, the metal sulfides can be divided in-to two categories

(i)   those which lose weight by evaporation of metal sulfide molecules and (ii) which are dissociated into sulfur and metal and then sulfur and metals evaporate .

PbS falls in the former category. Kellog [32] observed that substances with vapour pressure of the order of 80 mm of Hg should rapidly vaporize in a gas stream.

With the knowledge that PbS can be reduced [30] by H_2 and that PbS has an appreciable vapour presoure at practial temperatures (86 mm at $1100^{\circ}C$) development of a process

was sought by Cole et al [33] where PbS was vaporized from concentrate and reduced by hydrogen and the H_2S produced was processed to elementary sulfur form.

As PbS is substantially volatile, its volatilization characteristics are very important both from the point of view of vapour phase reduction as well as gas-solid reduction. Rao et al [34] very extensively studied the vaporization characteristics of PbS mixed with lime. They found that the kinetics of evaporation of PbS was much faster in helium than in nitrogen. Rapid vaporization of PbS in helium was attributed to higher diffusion rate of PbS (g) in helium than in nitrogen.

2.7 Choice of Lime as Scavenging Agent:-

In fact the scavenging capacity of lime for sulfur had been recognized long back. In 1951, T.Rosenquivst [22] made a detail thermodynamic study of the reaction $CaS+H_2O = CaO + H_2S$ and the desulfurization of liquid metal with lime. Later on, many investigators [2-10] have studied the scavanging capacity of various basic metal oxides. The equilibrium constant of scavanged reaction for various basic metal oxides at $827^{\circ}C$ is shown in Table 2.2 .

TABLE — 2.2

Equilibrium constants of scavenged reaction for various scavenging agents.

Reac^n. $M\Theta + H_2S \rightarrow MS + H_2O$ - - $k = P_{H_2O}/P_{H_2O}$
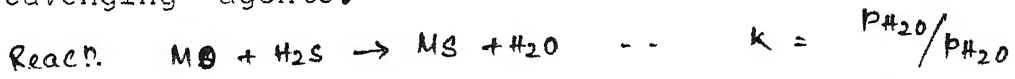
Scavenger	Equilibrium Constant
Na_2O	6.00×10^8
BaO	1.48×10^6
CaO	1.88×10^3
MnO	6.68×10^2
MgO	3.98×10^{-3}

Values compiled from Ref (37,38)

So from Table 2.2 it is obvious that according to the scavanging capability, Na_2O, CaO, BaO, MgO, MnO they may be arranged in the following manner.

Na_2O> BaO> CaO> MnO> MgO.
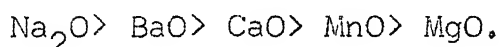
Though Na_2O and BaO have higher scavenging capacity than CaO but if one now considers the relative costs of these two reagents and their corrosiveness and consequent case of handling, lime is the obvious practical choice for commercial use of scavenged reduction process. It may be noted that lime has found favour as absorbent for sulfur-bearing gases generated in the new roasting procedure such as lime roasted process [7,8] basically aimed at containing atmospheric pollution.

Gavrilova and Allushuler[9] who investigated reaction between CaO and H_2S in temperature range 500 -1100°C, have found that reaction is rather slow at low temperature and is diffusion-controlled. Recently Habasi and Mikhail [10] have found that the scavanged reactionfollows parabolic rate equation and has an activation energy of 16.0 K.Cal/mole in the temperature range of 470° - 800°C.

The necessity of the above discussion about the scavenging capacity of various compounds and the scavenged reaction is to have proper validity of choosing lime for scavenging purpose and to have an idea about the thermodynamic

concept of the scavenged reaction before studying the

kinetic part.

It would become apparent from the literature
review presented in this chapter that the direct reduction of
metal sulfides in presence of lime has commercial implications
and that the direct reduction of lead sulfide with hydrogen
has not been investigated to any significant level. In the
present study an attempt has been made to examine the kinetics
of lime enhanced reduction of galena concentrate with hydrogen,
using the Thermogravimetric Analysistechnique. Since the lead
sulfide would have a substantially high vapour pressure at
the temperatures, to be employed for reduction studies, the
weight loss due to vaporization would be compounded with the
weight loss due to reduction. Keeping this idea in mind the
present work is divided in-to two parts. In the first part,
the vaporization kinetics of galena concentration,with various
proportions of lime added to it, has been studied at various
temperatures and nitrogen flow rates. The second part deals
with the reduction kinetics under various experimental condi-
tions specified in chapter 5.

CHAPTER -3

THERMODYNAMIC CONSIDERATION OF SCAVENGED REACTION

From the thermodynamic data available in litera-ture[35,36], it is possible to estimate free energy change, for the direct reduction reaction i.e.

$$PbS(s) + H_2(g) = Pb(\ell) + H_2S(g) \qquad \ldots\ldots\ldots (3.1)$$
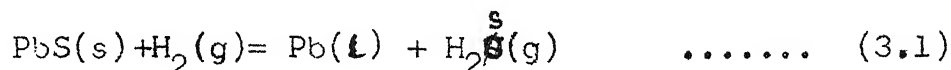
The calculated values of free energy change and the equilibrium constants for the above reaction (denoted by ΔG_1^0 and K_1 respectively) at various temperatures are tabulated in Table 3.1. From the ΔG_1^0 values it is apparent that the reaction (3.1) is not thermodynamically favourable and under standard conditions insignifcant reduction takes place even after prolonged treatment because of low value $(10^{-3} - 10^{-2})$ of equilibrium constant.

One of the ways of driving the reaction (3.1) forward would be to employ excessively high hydrogen flow rate, so as to sweep away the H_2S gas from the system. But this would obviously an inefficient and expensive method.

TABLE 3.1

Free energy change and equilibrium constant values for direct reduction, scavenging reaction and scavenged reduction reaction at various temperatures.

Reaction

(1) $PbS(s)+H_2(g)=Pb(l)+H_2S(g)$ ΔG^0_1

(2) $CaO(s)+H_2S(g)=CaS(s)+H_2O(g)$ ΔG^0_2

(3) $PbS(s)+CaO(s)+H_2(g)$
    $=Pb(l)+CaS(s)+H_2O(g)$ ΔG^0_3

Equilibrium constants

$K_1 = P_{H_2S}/P_{H_2}$

$K_2 = P_{H_2O}/P_{H_2S}$

$K_3 = P_{H_2O}/P_{H_2}$

Temperature (°C)	ΔG^0_1	ΔG^0_2	ΔG^0_3	K_1	K_2	K_3
527	10109.96	−15028.26	−4918.09	1.802×10^{-3}	1.2×10^{-4}	21.624
627	9356.226	−15100.85	−5744.58	5.528×10^{-3}	4.4×10^{-3}	24.3232
727	8620.00	−15045.88	−6425.35	1.343×10^{-2}	1.85×10^{-3}	24.8455
827	7899.55	−14987.16	−7087.70	2.758×10^{-2}	9.09×10^{-2}	25.072
927	7193.44	−14943.69	−7750.09	4.992×10^{-2}	5.06×10^{-2}	25.2595

Values compiled from Ref (36),

Reduction By Hydrogen in Presence of a H_2S Scavenger.

A better way of achiving the desired low P_{H_2S} value level for driving reaction (3.1) forward is to employ a scavenging compound which when placed near the reacting sulfide particle is capable of rapidly and efficiently absorbing H_2S as soon as it is formed. If lime is used as the scavenging compound, it would react with H_2S in the following manner

$$CaO(s) + H_2S(g) = CaS(s) + H_2O (g) \qquad \ldots.3.2$$
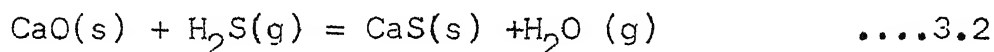
The maintenance of an extremely low in situ P_{H_2S} value by the use of a suitable scavenger will perhaps enable the reaction to proceed forward.

The scaveng·d direct reduction of lead sulfide will take place in the following manner.

$$PbS(s) + CaO(s) + H_2 (g) = Pb(\ell) + CaS (s) + H_2O (g)$$
$$\ldots. 3.3$$
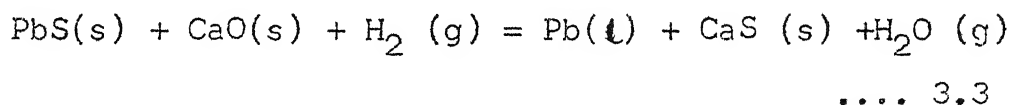
The change of free energy for the above two reactions (denoted by ΔG_2^o and ΔG_3^o respectively) along with the equilibrium constant values (denoted by K_2 and K_3 respectively) at various temperatures are given in Table 3.1 .

One aspect which might complicate the reduction process is the possibility of oxidation of the reduced metal by the water vapour. However the comparison of equilibrium

(P_{H_2O}/ P_{H_2}) constant values (Table 3.2) for reaction 3.4 viz

$$MO(s) + H_2 = M(s) + H_2O (g) \qquad ....3.4$$
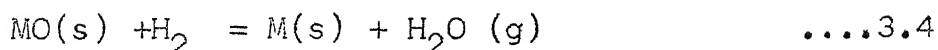
with those for the reaction (3.3) suggests that the oxidation of metallic lead with water vapour can be ignored.

Tbale 3.2: — Comparison of equilibrium constants for lime scavenged reduction reaction with corresponding values in oxide reduction for lead.

Reactions:- $PbS(s) + CaO (s) + H_2(g) = Pb(l) + CaS(s) + H_2O$

$$....3.3 ..K_3$$

$$PbO (s) + H_2(g) = Pb(l) + H_2O (g) \quad ....3.4.. K_4$$
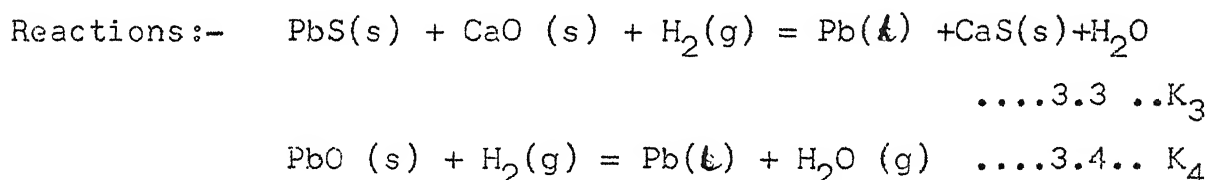
Tmperature ($^{\circ}$K)	Equilibrium constants	
	K_3	K_4
700		3.23×10^4
800	21.624	2.03×10^4
900	24.3232	1.38×10^4
1000	24.8455	9.99×10^3
1100	25.0702	7.61×10^3

CHAPTER - 4

EXPERIMENTAL

As already mentioned towards the end of Chapter 2, the present investigation has been divided into two parts,

(i) effects of temperature, lime content and nitrogen flow rate on the evaporation characteristics of galena concentrate

(ii) reduction of cylindrical pellets of galena under various experimental conditions.

In this chapter, brief drescriptions of materials employed in the investigation, experimental set up and experimental procedure are presented.

4.1 Materials:-

(A) Galena concentrate:- The galena concentrate was procured from Hindusthan Zinc Limited, Udaypur. The chemical composition of the concentrate is given in Table (4.1).

TABLE 4.1 :- Chemical Composition of the concentrate.

Constituent	wt%
Pb	56.7
Fe	2.1
Zn	7.6
SiO_2	6.0
S	15.37

To verify the phases present in the concentrate, X-ray analysis was carried out and the presence of PbS, ZnS, SiO_2 was confirmed.

Concentrate having particle size of -100 mesh was used in this investigation .

(B) Lime:- Commercial grade lime having particle size -120 mesh was employed for the present study. This lime was obtained from Satana mines , M.P.

2 Experimental Set up:-

Both evaporation and reduction studies were carried out using Thermogravimetric Analysis (TGA). The schematic diagram of the experimental set up is given in Fig. 4.1 . It comprised of a Kanthal-A wire wound electric resistance vertical long tube furnace, enclosing an inner diameter of 5cm fused Mullite tube which served as a reaction chamber. Both the inert and the reducing gases could be admitted through the gas inlet at the bottom of the furnace, and the out coming gases withdrawn from the top of the furnace . The top end of the reaction tube was fitted with a brass head stopper with O- ring which made this end of the reactor air tight. Provision was there to cool this brass head stopper by flowing cold water through a brass coil surrounding the brass head. A. Chromel alumel thermocouple, introduced from
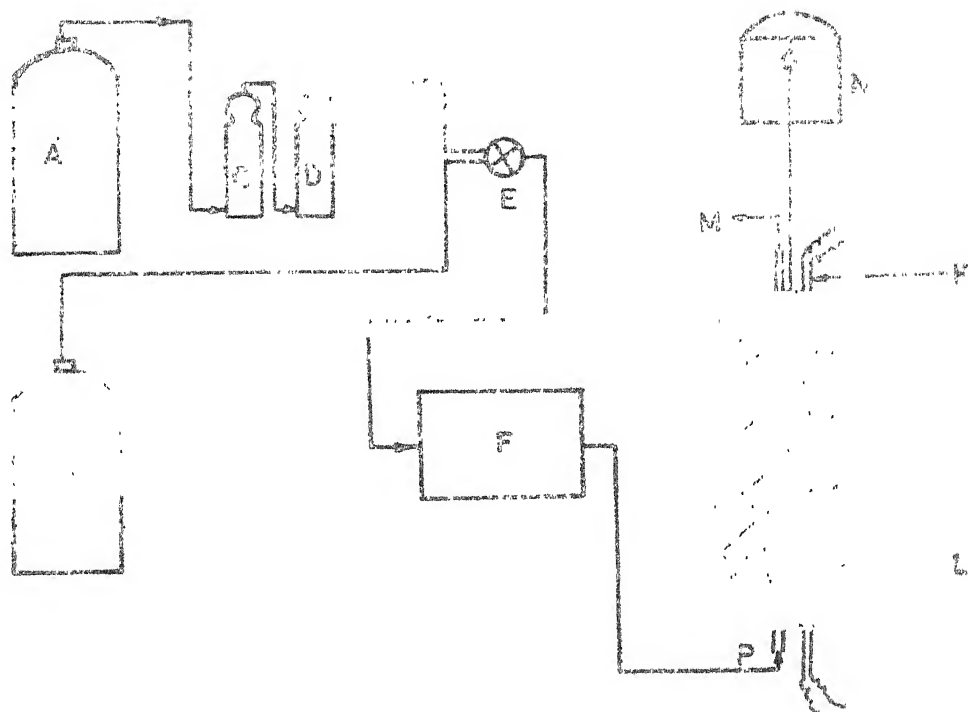
Fig. 4.1

A H_2 gas cylinder

B N_2 gas cylinder

C, D   Anhydrous $CaCl_2$

E   Stop cock

F   Copper gauge furnace

G   Reaction Tube

H   Furnace

I   Sample Holder

J   Sample

K, L   Thermocouples

M   gas outlet

N   Single pan balance

O   Temperature Controller

P   Gas inlet

the bottom of the furnace was used for controlling the temperature of the furnace. A steel wire mesh container served as the sample holder. This could be suspended freely into the reactor with the help of a canthal wire which passed through a hole in the brass head stopper. The other end of this wire was attached to a semi-automatic single pan mettler balance. Furnace temperature could be held constant using an automatic Electromax controller. The efficiency of the controlling unit was found to be $\pm 2^{o}C$. A constant temperature zone of about 6 cm length near the middle of the reaction tube was obtained. A gas purification train consisting of columns of anhydrous $CaCl_2$ and a copper gauge furnace was designed. To measure the gas flow rates, capilary flow meters were employed.

4.3 Preparation of Pellets:-

Cylindrical pellets of 0.5 inch. diameter and length varying from .8-1.4 inch were used in the evaporation and reduction studies. The ratio of lime to galena (R) in these pellets was varied from 0 to 4 . To make the pellets of various R values, required amounts of galena concente and lime were weighed accurately. The weight of the mixture was kept constant to about 5 gm. After thorough mixing of the two poweders, the powder mixture was pressed in 1/2 inch steel die at 20 Kil/o Newton pressure (load) using a standard motor operated pressing unit.

The porosity of the pressed samples could be estimated using the values of the true density of the powder and the apparent density of the powder in the pellet. The former was determined using the specific gravity bottles and Kerosene as the liquid while the later was obtained from the weight and dimension of the compacted pellet. A sample calculation and the results of the density measurements are given in Appendix 1. Variation of porosity of pellets as a function of lime content is given is Table 4.2,

TABLE 4.2:- Porosity of pellets with various R valus.

R	Porosity
0	10.84%
1	11.27%
2	12.56%
3	14.12%
4	16.91%

Experimental Procedure :-

Evaporation:

The evaporation experiments using compacted pellets of various compositions were carried out at various temperature and nitrogen flow rates. Experimental conditions employed in this study are tabulated in Table 4.3 .

To study the evaporation at constant temperature, the copper gauge furnace and the reactor were gradually heated to the desired temperature. When the temperature was stabilized a pellet of known weight and porosity was kept into the sample holder and introduced into the reaction chamber but held near the top end of the furnace tube. The brass head was carefully tightened and then the gas train and the reaction chamber were flushed with nitrogen. Once the reaction chamber was free from air, the nitrogen gas flow rate was set at the desired flow rate value. After steady state, with respect to the gas flow rate was attained the pellet was lowered to the maximum temperature zone. Weight of the sample holder and the pellet was immediately measured and taken as the initial weight of the sample . A chromel-alumel thermocouple tip which was kept very near to the sample holder recorded the furnace temperature which was assumed to be the same as that of the pellet. The change in weight as function of time was recorded at regular interval of time with the help of the single pan balance. All experiments were conducted for 60 minutes after which the samples were

pulled up and cooled in nitrogen atmosphere before removing from the furnace.

A few experiments were repeated to check the reproducibility of the data and the variation in results was found to be within 2.0%

1.4 (b) Reduction :-

The reduction experiments were carried out in the same set up described above using almost the same procedure as in the case of evaporation studies. The only difference was that after flushing the furnace with nitrogen and introduction of the pellet to the furnace, the nitrogen gas was injected at a predetermined flow rate, for about 10 minutes after which nitrogen gas supply was switched off and the reducing gas was introduced at a predetermined flow rate. The reduction experiments were carried out for 60 minutes. Before taking out the pellet, the furnace chamber was again flushed with nitrogen to drive away unconsumed hydrogen. Then the pellet was slowly brought to the cooler part of the furnance and ultimately taken out for immediate transfer to desiccator to cool it down to room temperature. Various experimental conditions which were employed in this part of the study are tabulated in Table 4.4

TABLE 4.3

Conditions of evaporation experiments

Temperature $^\circ$C	Composition	Nitrogen Flow Rates C.C./ min.
	R=0	200
		400
		600
	R=1	200
		400
		600
650	R=2	200
		400
		600
	R=4	200
		400
		600
	R=0	200
		400
		600
700	R=1	200
		400
		600

Contd... TABLE 4.3

Conditions of evaporation experiments

Temperature °C	Composition	Nitrogen Flow Rates C.C./min
		200
	R=2	400
		600
		200
700	R=3	400
		600
		200
	R=4	400
		600
		200
	R=0	400
		600
		200
750	R=1	400
		600
		200
	R=2	400
		600

Contd... TABLE -4.3

Conditions of evaporation experiments

Temperature °C	Composition	Nitrogen Flow Rates C.C./min
750	R=4	200
		400
		600
800	R=0	200
		400
		600
	R=1	200
		400
		600
	R=2	200
		400
		600
	R=4	200
		400
		600

Contd...TABLE-4.3

Conditions of evaporation experiments with pellet made
from residue after leaching (10% HCl) of galena concentrate

Temperature °C	Composition	Nitrogen Flow Rates C.C./min.
700	R=0	400
700	R=1	400

TABLE – 4.4

Conditions of reduction experiments

Temperature °C	Composition	Hydrogen Flow Rate C.C./min.
600	R=0	300
		150
	R=0	
		300
		150
	R=1	
650		300
		150
	R=2	
		300
		150
	R=4	
		300
		150
	R=0	
700		300
		150
	R=1	
		300

Contd... TABLE -4.4

Conditions of reduction experiments

Temperature °C	Composition	Hydrogen Flow Rate C.C./min.
		150
	R=2	
700		300
		150
	R=3	
		300
		150
	R=0	
750		300
		150
	R=2	
		300
	R=0	150
800		
	R=1	1500

Contd... TABLE - 4.4

Condition of reduction experiments with pellet made from
residue after leaching (10% HCl) of galena concentrate

Temperature °C	Composition	Hydrogen Flow Rate C.C./min.
700	R=1	200

Various techniques were tried to directly measure the amount of lead present in the reduced samples. These included

(i) Chemical analysis of reduced sample to separately analyse metallic Pb and residual PbS in the sample

(ii) Melting of reduced sample in a vaccum sealed quartz capsule to separate Pb

(iii) X-ray analysis of the reduced sample

(iv) Estimation of residual sulfur

None of these technique however worked to satisfaction . The details of some of these techniques and the reason for their failure are given in Appendix 4 X-ray analysis, infact, was used satisfactorily for qualitative analysis.

CHAPTER -5

RESULT AND DISCUSSION

5.1   Kinetics of Vaporization of Galena in Nitrogen
       Atmosphere :-

        Vaporization of galena with and without lime
was investigated at four different temperatures, namely
$650^{\circ}C$, $700^{\circ}C$, $750^{\circ}C$, $800^{\circ}C$.   At each temperature samples
of different composition (R=0,1,2,4) were subjected to
vaporization.   Three different flow rates viz.   200 c.c/min,
400 c.c/min and 600 c.c/ min were employed. Experimental
conditions which were used in this part of study have already
been listed in Table (4.3).

        The basic kinetic data consisted of weightloss
of galena samples at regular interval of time.   The % weight
loss vs. time plots for various samples at these various exper-
imental conditions are presented in Fig. 5.1 -5.4.

        It can be seen from the figures that at lower
temperatures ($650^{\circ}C$, $700^{\circ}C$) all the % weight loss vs. time
plots remain almost linear for all values of flow rate and
lime content.   At higher temperatures ($750^{\circ}C$ and $800^{\circ}C$) the
plots remain almost linear for experiments where no lime was
used , but with the addition of lime, the linear character
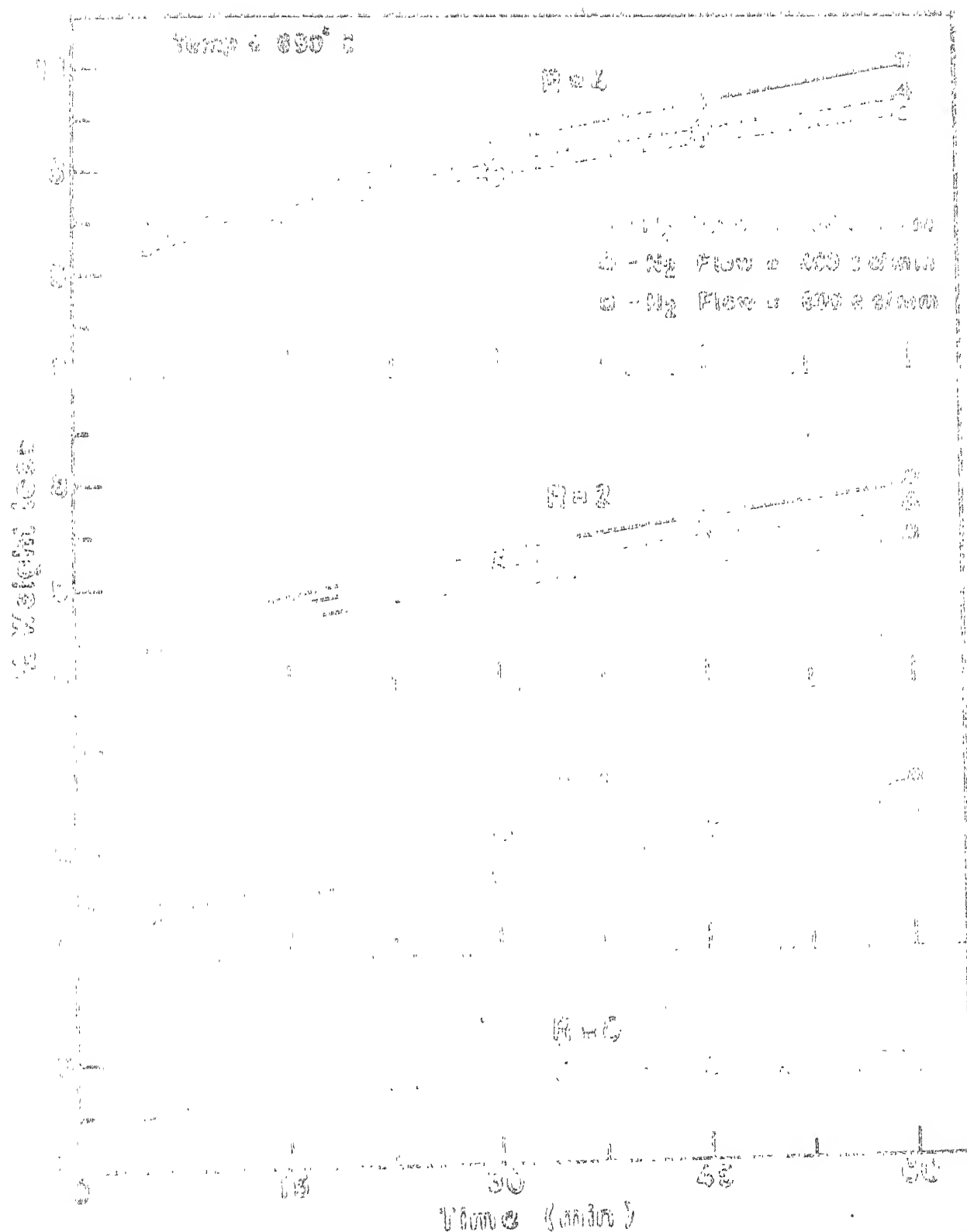
Fig. 6.1   ... of ... at 850°C
at various N₂ flow rates for pellets having
... lime to ... ratios (R).

△ = Mg 1234

☐ = Mg 1412

R = 2

R = 2

R = 1

R = 0

Time (min)

0   15   30   45   60

Fig.3.2 Sensitivity of gettering rate at 700°C at
         constant N_2 flow rates for varying
         time to gettering ratio (R).

FIG.5.3 Evaporation of galena concentrate at 750°C at various N₂ flow rates for pellets having various lime to galena ratios (R).
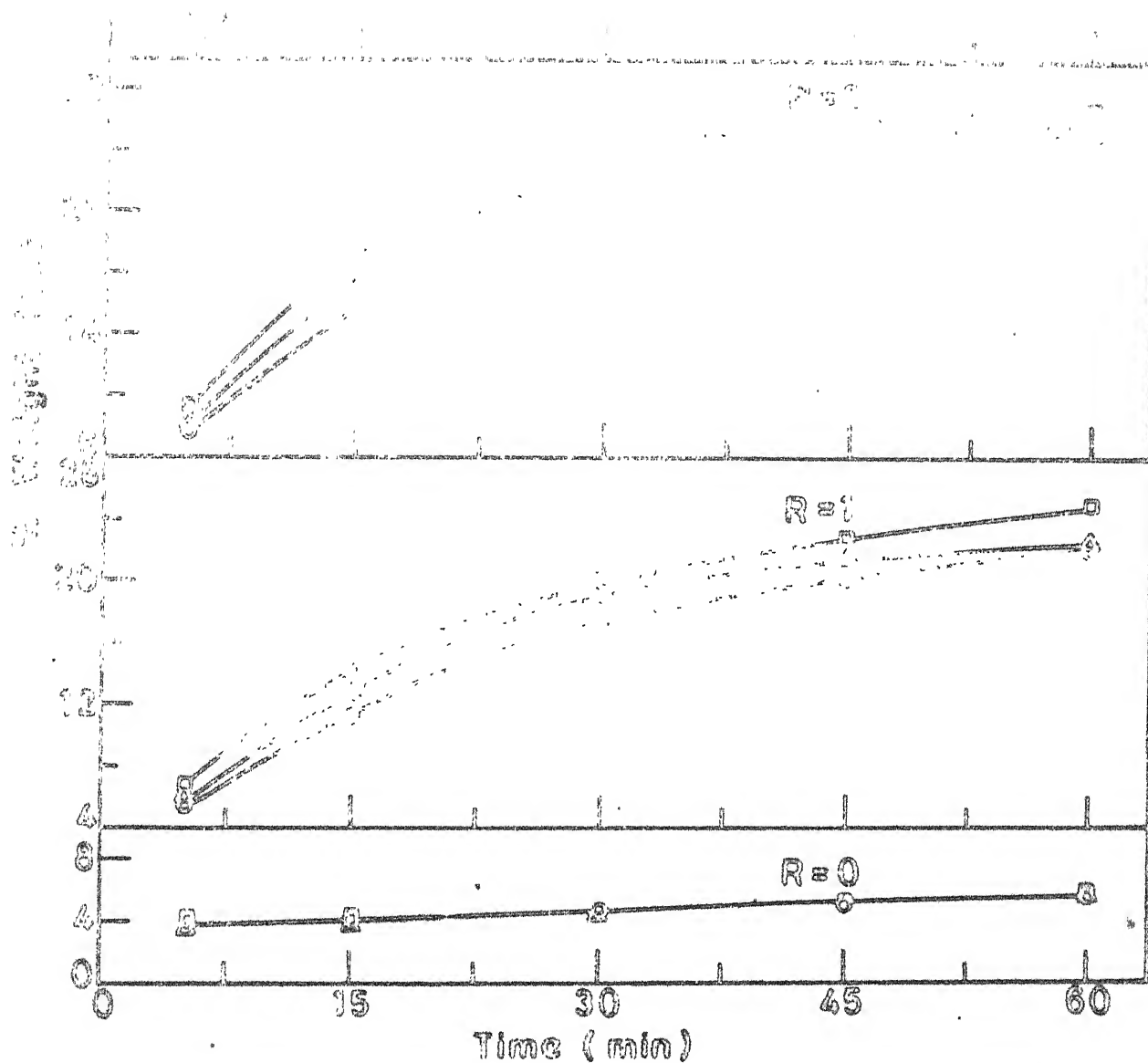
Fig.3.4 Evaporation of gallium concentrate at 800°C at various N_2 flow rates for acetate having various lime to gallium ratios (R).

of these plots changed.

5.1.1 Effect of temperature:- As expected, the amount of galena evaporated increased with increasing temperature.

The equilibrium vapor pressure of lead sulfide (Pce) can be computed from the standard free energy equation given below[34]

$$G^o(J) = -RT \ln Pce = 254596 + 15.51 \ T \log T + 8.23 \times 10^{-3} T^2$$
$$- 229.12 \ T$$

The calculated Pce values at various temperatures of interest are tabulated in Table 5.1

TABLE 5.1 Equilibrium Vapor Pressure values for
PbS at various Experimental Temperatures.

Temperature (oC)	Vapor Pressure (atm)
650	5.76×10^{-6}
700	2.89×10^{-5}
750	1.229×10^{-4}
800	4.54×10^{-4}

It is evident from Table 5.1 that the equilibrium vapor pressure of PbS increases with temperature and hence vaporization.

5.1.2 Effect of Gas Flow Rate:- In general, the vaporization process may be represented by the following reversible reaction,

$$PbS\ (s) \rightleftharpoons PbS\ (g)$$
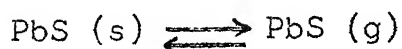
For the process to continue it is required that the gases produced be continuously removed from the pellet surface to the bulk of the surrounding gaseous phase. This involves the mass transfer of the gaseous species through the concentration boundary layer thickness and the pellet. The mass flow is inversely proportional to the boundary layer thickness which depends on the gas velocity. Decreased boundary layer thickness with increasing gas velocity (Volume flow rate) would result in faster rate of mass transfer and hence enhanced rate of vaporization.

Effect of gas flow rate on vaporization rate for pellets containing varying amount of lime is shown in Figs. 5.1 to 5.4 . It may be seen that in general, the vaporization increases with increasing gas flow rate in all pellets containing lime but this effect is not that apparent in the case of pellets without lime.

5.1.3 Effect of Lime:-

The reason for adding lime to galena for the vaporization studies was to get some idea about the vaporization characteristics of the pellets of same compositions which were to be later used in the reduction studies. It is

evident from Fig. 5.1 to 5.4 that for the same conditions
of temperature and gas flow rate the vaporization increases
with increasing lime content. From the porosity measurements
it was found that the addition of lime resulted in increased
porosity of the pellets (Table 4.2). Lime could also disperse
the galena particles throughout the matrix and thus prevent
them from getting sintered during the reaction. Increased
porosity of pellets and prevention of sintering results in
larger exposed surface of the galena particles from which
the vaporization would take place.

5.1.4   Evaluation of Rate Constant and Activation Energy of
        Vaporization:-

The rate constant of vaporization under nitrogen
atmosphere (k_{v,N_2}) was evaluated for each experiment using
the relation

$$k_{v,N_2} = \frac{1}{W^o_{PbS}} \left(\frac{d \Delta W^o_{PbS}}{dt} \right)$$

$$=(\text{ Slope of \%wt. loss vs. time plot})x \frac{W^o_{PbS}}{100}$$

......(5.1)

where ΔW^o_{PbS} is the weight loss in the interval of time t
and W^o_{PbS} is the initial weight of galena in the sample. The
amount of PbS present in the sample could be found out

for various compositions by using the following relations

for   R=1 W^{O}_{PbS} = 0.5 W^{O}_{T}

        R=2 W^{O}_{PbS} = 0.33 W^{O}_{T}

        R=3 W^{O}_{PbS} = 0.25 W^{O}_{T}

        R=4 W^{O}_{PbS} = 0.2 W^{O}_{T}

Where W^{O}_{T} is the total weight of the sample. Slope in Eq. 5.1 represents a time average of the slope of % wt. loss vs. time plots in Fig. 5.1 to 5.4. The rate constant values for various experimental condition are tabulated in Table 5.2.

The rate constant data at various conditions would be used for calculating the activation energy values using Arrhenius type of plot. Log k_{v,N_2} vs. $\frac{1}{T}$ plot for different gas flow rates and R values are shown in Fig.5.5. Activation energy values were evaluated from the slope of the linear plot in this Figure.

E = - R x Slope

Were R is the universal gas constant. Activation energy values as a function of gas flow rates and lime content are tabulated in Table 5.3.

It is evident from Table 5.3 that for a given flow rate there is not much variation in activation energy with variation in lime content. It is attributed to the
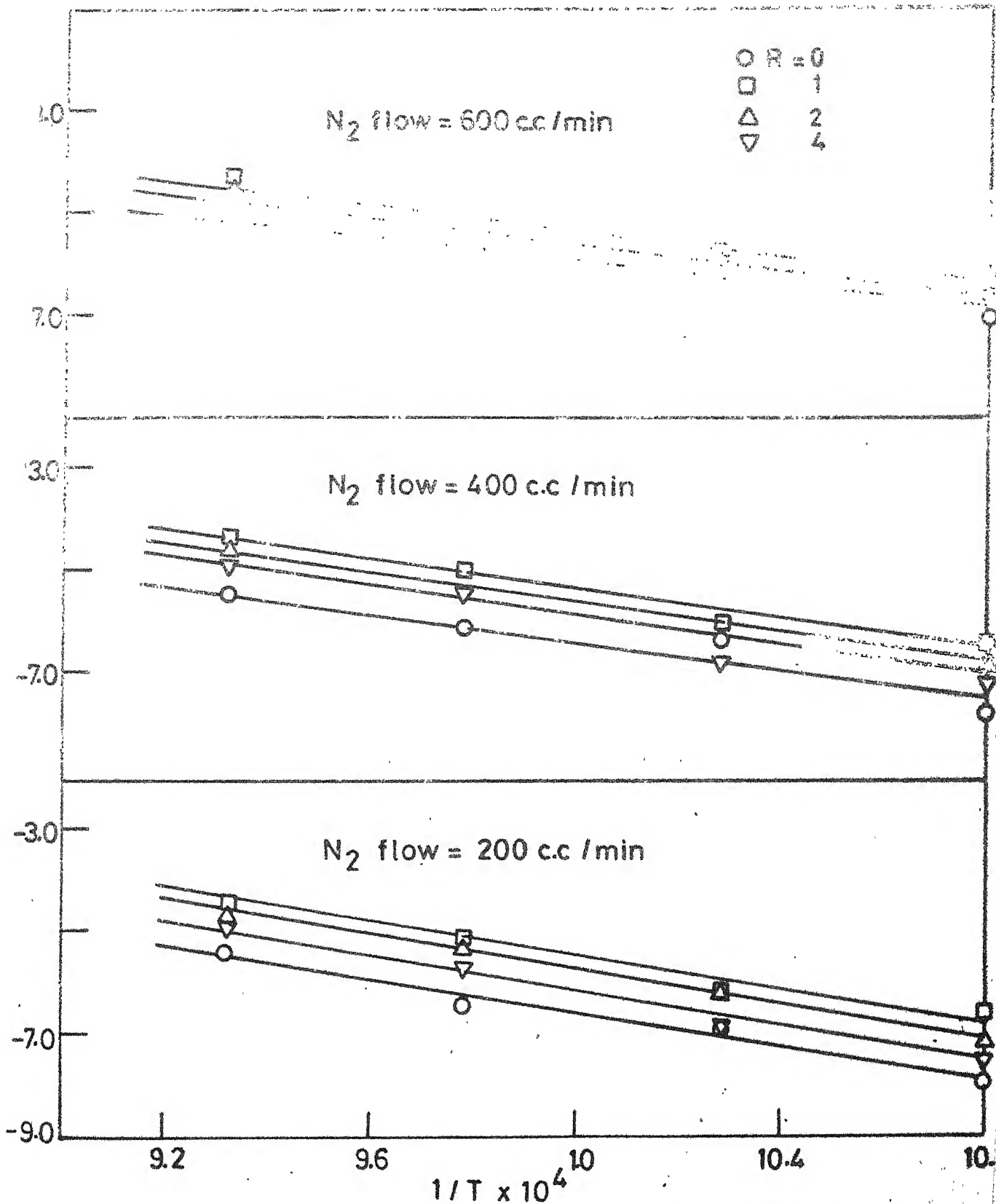
Fig. 5.5. Activation energy of vaporization of galena under various conditions.

TABLE -5.2   Rate   constant values for vaporization

under various experimental conditions

Temperature °C	Composition	Flow rate c.c/min	k_{v,N_2} min^{-1}
		200	3.744×10^{-4}
	R=0	400	4.26×10^{-4}
		600	4.77×10^{-4}
		200	1.334×10^{-3}
	R=1	400	1.595×10^{-3}
		600	1.740×10^{-3}
650		200	7.810×10^{-4}
	R=2	400	1.084×10^{-3}
		600	1.189×10^{-3}
		200	6.120×10^{-4}
	R=4	400	7.164×10^{-4}
		600	8.517×10^{-4}
		200	9.916×10^{-4}
700	R=0	400	1.652×10^{-3}
		600	1.817×10^{-3}

Contd...

Contd.... TABLE -5.2

Temperature $^{\circ}C$	Composition	Flow rate c.c/min	k_{v,N_2} min^{-1}
		200	2.019×10^{-3}
	R=1	400	2.369×10^{-3}
		600	2.736×10^{-3}
		200	1.813×10^{-3}
700	R=2	400	1.948×10^{-3}
		600	1.997×10^{-3}
		200	9.475×10^{-4}
	R=4	400	1.014×10^{-3}
		600	1.159×10^{-3}
		200	1.591×10^{-3}
	R=0	400	2.106×10^{-3}
		600	2.182×10^{-3}
		200	5.540×10^{-3}
	R=1	400	6.216×10^{-3}
750		600	6.574×10^{-3}
		200	5.072×10^{-3}
	R=2	400	6.149×10^{-3}
		600	7.331×10^{-3}

Contd...

Contd... TABLE-5.2

Temperature $^{\circ}C$	Composition	Flow rate c.c/min	k_{v,N_2} min^{-1}
750	R=4	200	3.549×10^{-3}
		400	4.574×10^{-3}
		600	4.654×10^{-3}
800	R=0	200	4.222×10^{-3}
		400	4.228×10^{-3}
		600	8.101×10^{-3}
	R=1	200	1.107×10^{-2}
		400	1.257×10^{-2}
		600	1.371×10^{-2}
	R=2	200	9.258×10^{-3}
		400	9.020×10^{-3}
		600	1.017×10^{-2}
	R=4	200	6.671×10^{-3}
		400	7.562×10^{-3}
		600	3.053×10^{-3}

TABLE 5.3

Activation energy of vaporization of galena having various lime to galena ratio (R) at various nitrogen flow rate.

Flow rate c.c./min.	Composition	Activation energy K.cal/mole
	R = 0	30.8
	R = 1	30.42
200	R = 2	29.87
	R = 4	29.63
	R = 0	26.3
	R = 1	26.12
400	R = 2	25.82
	R = 4	25.75
	R = 0	22.85
600	R = 1	22.42
	R = 2	22.01

fact that the addition of lime does not alter the basic mechanism of vaporization. The enhanced rate of vaporization with increased lime content is due to the increased exposed surface of the galena particles which is reflected in the increased value of the prexponential terms in the Arrhenius equation.

Reduction of activation energy with increased gas flow rate (Table 5.3) indicates that the flushing of vapor by the flowing gas reduces the resistance to the mass transfer through the boundary layer.

The activation energy values obtained in our study,however are somewhat lower than those obtained by EL- Rahaiby and Rao [34] who reported activation energy of vaporization of lead sulfide as 52 K. Cal/mole. The apparent discrepancy in these values may be due to the fact that the starting material in the present study was galena and not pure lead sulfide. Further in the case of Rahaiby and Rao, the vaporization was only from one surface which was enveloped by a stagnant layer of an inert gas unlike ours where the vaporization was from the entire surface of the pellet exposed to a flowing gas.

5.2   Kinetics of Reduction of Galena in Hydrogen.

Reduction of galena with and without lime was investigated at four different temperatures. At each temperature samples of different compositions and flow rates of H_2 were employed. All the experimental conditions used in this part of study have already been listed in Table 4.4.

The basic kinetic data consisted of weight loss of galena at regular interval of time. It may be recognized that the total weight loss as measured by using the Thermogravematric Analysis, would be due to the following two factors

(i)   The weight loss due to vaporization in flowing hydrogen gas

(ii)   The weight loss due to the reduction of lead sulfide with hydrogen

Therefore to be able to estimate the weight loss due to the reduction only it is required to estimate the weight loss due to vaporization. As a first approximation it was assumed that the vaporization characteristics of galena in hydrogen would be identical to those of in nitrogen. Therefore, using the weight loss data obtained in the previous section of this chapter, an attempt was made to estimate the weight loss due to the reduction reaction only.

A typical plot superimposing weight loss due to the vaporization of galena in nitrogen on the plot of total weight loss in hydrogen as a function of lime is shown in Fig. 5.6. Using such plots for all our experiments it could be possible to estimate the percent weight loss due to reduction only. Since in each of the reduction experiments, nitrogen was injected for 10 minutes before the hydrogen flow started, the weight of the sample after 10 minutes was taken as the starting weight in all the computations.

Results of the calculations are presented in Appendix (2) . Percent weight loss due to the reduction versus time plots at various temperatures for different compositions of the starting galena pellets (R=0,1,2,4) are shown in Figs. 5.7 to 5.9.

5.2.1 Effect of Flow Rate: _

The fact that the extent of reduction was higher at higher flow rate of the reducing gas at a given temperature for the same composition of the galena lime samples,is evident from Fig. 5.7 to 5.9 . It is well known that increasing gas flow rate decreases the resistance to mass transfer through the gas film surrounding the particle. If the mass transfer through the gas film is the rate controlling step, which indeed is at low gas flow rates,
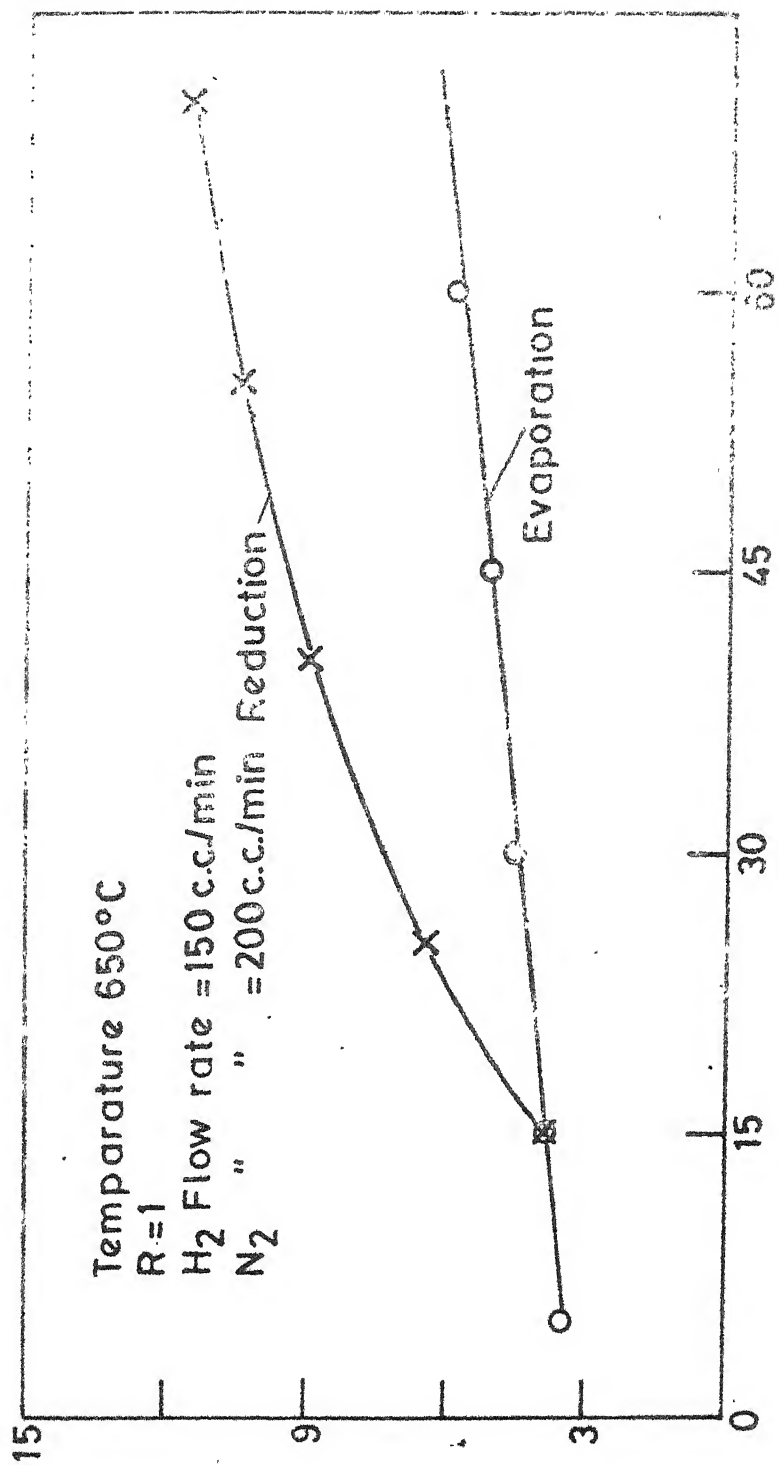
Fig. 5.6. Typical plot to calculate reduction wt. loss of metal by using on evaporation plot.
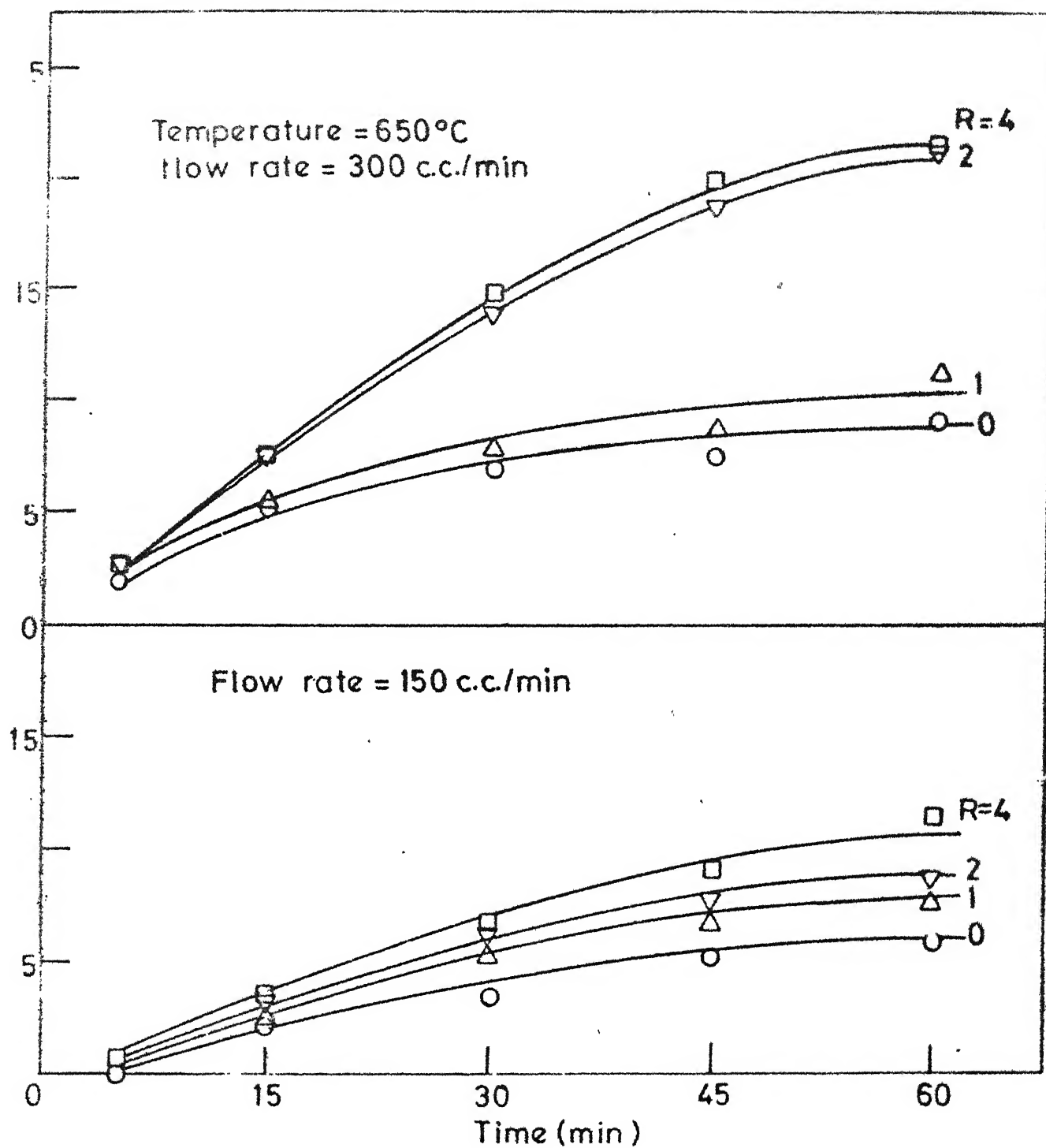
Fig. 5.7. Weight loss of alumina at 650°C temperature at various H$_2$ flow rates for pellets having different compositions.

Temperature 700°C
Flow rate = 300cc/min

Flow rate = 150 c.c./min

Time (min)
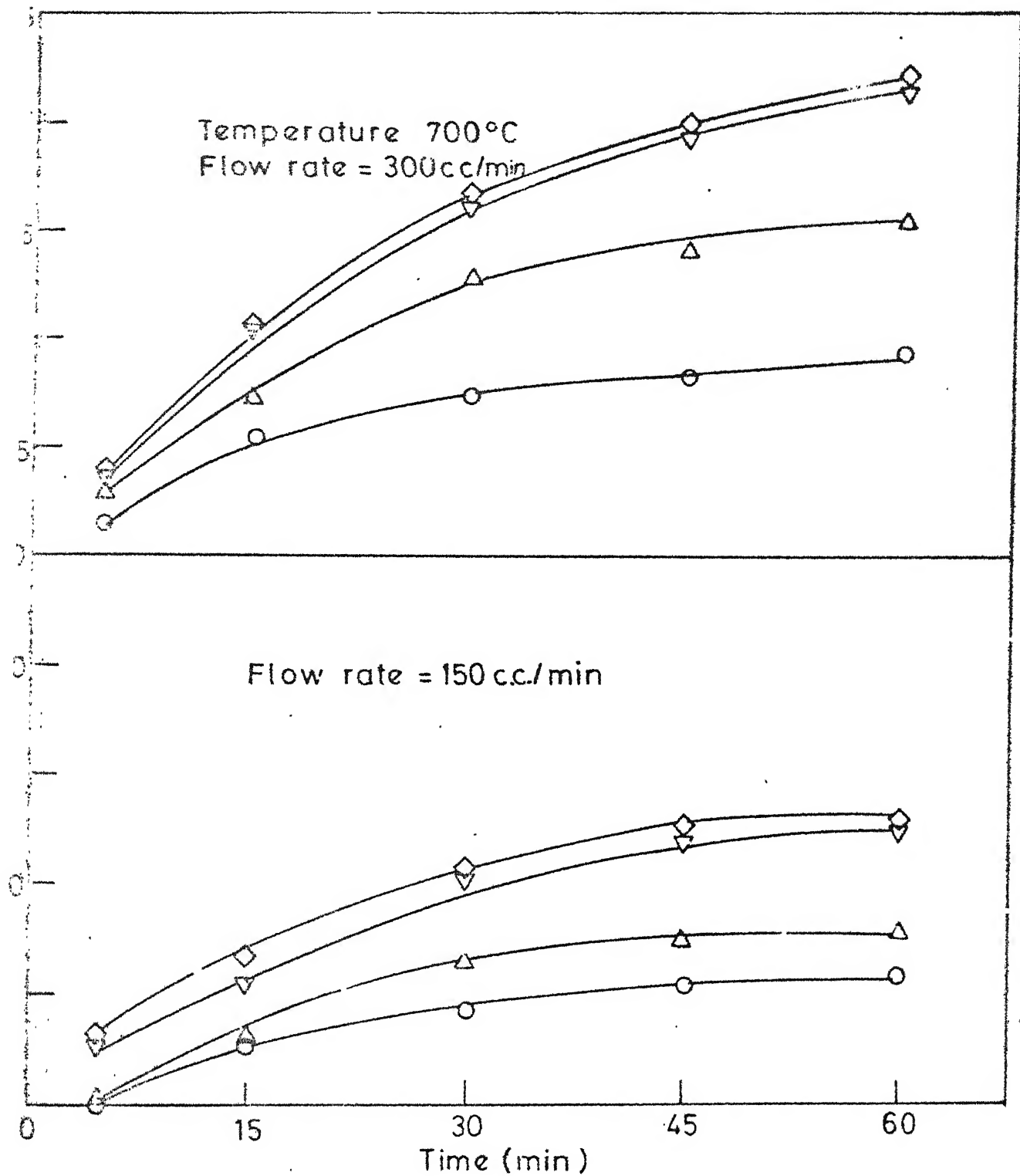
weight loss of minera at 7 °C temperature at various
flow rates for pellets having different compositions.
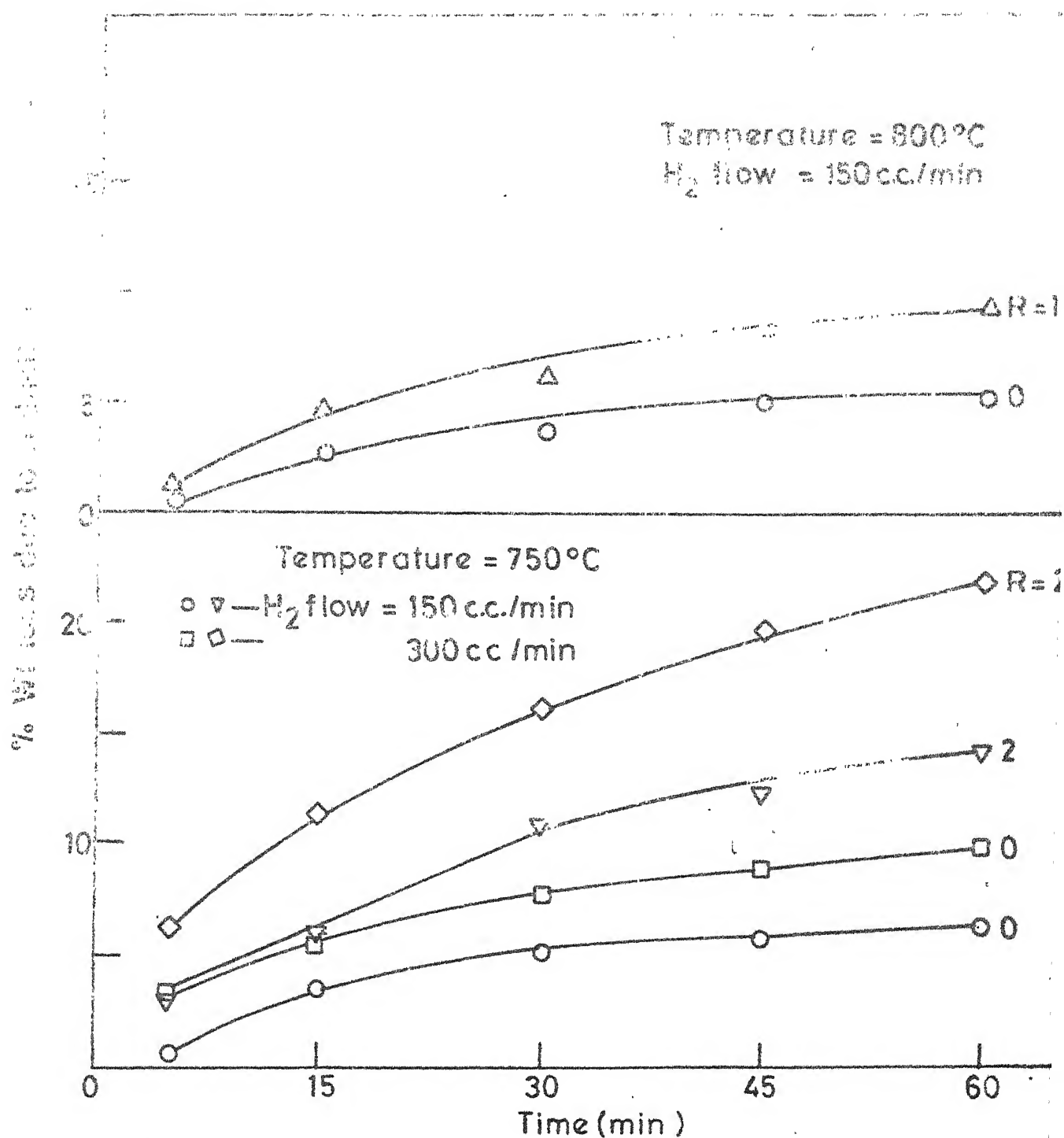
Fig. 5.9 Weight loss of galena at 750 & 800°C temperature at various
H₂ flow rates for pellets having different compositions.

the rate of reaction would increase with increasing gas flow rate. In our case, since low gas flow rates were involved, we would expect the mass transfer through the gas film to be the rate controlling step. Hence, the extent of reduction would be higher at a higher gas flow rate.

5.2.2 Effect of Temperature:

No clear-cut effect of temperature is observed in Fig. 5.7 to 5.9. Reduction tends to increase with temperature upto about $750^{\circ}C$ and then it decreases. Percent weight loss estimated at $800^{\circ}C$ is lower than those measured at lower temperatures. There are two possible reasons for the observation.

(i) High temperature leads to sintering of lead sulphide particles which results in lowering of surface area of the particles.

(ii) Lead sulphide reacts with lime to form a complex compound which has a lower reducibility.

However, the exact reason could not be ascertained.

5.2.3 Effect of lime:

As it has been shown in chapter 3, also, even thermodynamically, reduction of PbS with hydrogen is enhanced with lime. All our experimental observations

Figs. 5.7 to 5.9 also support this fact. At all temperatures the rate of reduction increases with increasing lime constant. These are, however, a few interesting observations

(i)   The plots corresponding to R=O and R= 1 are some what close to each other. Whereas the gap between plots for R= 1 and R= 2 is comparatively larger.

(ii)   The plots corresponding to R= 2 and R= 3 or 4 tend to overlap, except in the plot at 650°C and 150 c.c / min. flow rate .

It is possible to explain some of the observations if one analyses the reduction mechanism carefully. In the case of galena samples without lime ,the reduction of lead sulfide will proceed according to the following reaction

$$PbS + H_2 \longrightarrow Pb + H_2S \qquad\qquad ....(5a)$$
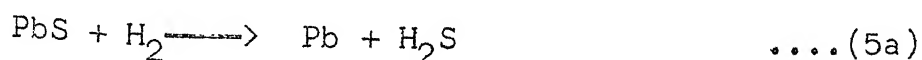
whereas in case of galena samples containing lime ,the reaction will be

$$PbS + H_2 + CaO \longrightarrow Pb + CaS + H_2O \qquad .....(5b)$$
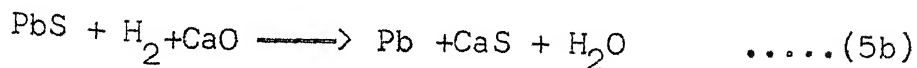
It is to be noted that in the case of the galena the weight loss on reduction of one mole of galena will correspond to the loss of one atom of sulfur whereas in the case of latter it would correspond to the loss of one atom of oxygen. It is thus obvious that for the same extent of reaction, the lime

free galena samples would exhibit exactly   twice the
weight loss in galena samples containing lime.

To verify that the reduction of galena was indeed
through the above two reactions, a simple test was carried out.
Outgoing gases from the reactor, after cooling, were passed
through $CdCl_2$ solution. It was observed that in the case of
lime free galena sample, thick black precipitate of CdS was
formed as a result of the following reaction.

$$CdCl_2 + H_2S \longrightarrow CdS + 2HCl \qquad\qquad ...(5c)$$
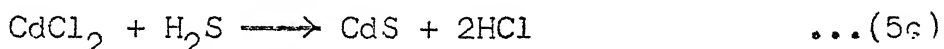
In the case of galena samples with R=1, also the black preci-
pitate was observed but its amount was much less. For galena
samples with R>2 no precipitate was observed, clearly indica-
ting that all the released sulfur was taken up by lime to
form CdS and, therefore the reduction of galena in presence of
lime took place according to the Reaction (5b). In the case
with R= 1 it seems some galena was directly reduced, though
the major fraction was reduced by the Reaction (5b) . These
observations have also been substantiated by X-ray analysis
of the reduced samples presented in Appendix(5). In the
case of samples with R= 0, the phase which could easily be
identified included galena, lead ,whereas in the case of
lime containing samples calcium sulfide was present in
substantial quantities.

It is expected that there would be an optimum
amount of lime which would correspond to the amount which is
sufficient to scavenge the total sulfur that could be released
due to the reduction reaction. Excess lime therefore, should
not have any significant effect on the reduction reaction.
Minor effects, however, may be there due to minor differences
in physical characteristics of the samples having varying
amount of lime.

There was however, one major flaw with the above
analysis. In many cases the percentage weight loss due to
reduction exceeded the theoretical percent weight loss required
for 100% reduction of lead sulfide . There could be two reas-
ons for this discrepancy.

(i)   Some of the lead that is formed as a result of the
reduction reaction is also vaporized. It may be mentioned
that the melting point of lead is only 327°C and that its
vapor pressure at temperature employed in this investigation
would be high enough to cause observable weight loss.

(ii) The assumption that the vaporization characteristics of
lead sulfide in hydrogen are identical to those in nitrogen
is not valid.

As it was not possible to exclusively measure the vaporization of galena in hydrogen (without causing reduction), an indirect method was used to estimate the vaporization rate in hydrogen. The method is described below.

5.2.4 Estimation of Vaporization Rate of Galena in Hydrogen:

It is assumed that the rate of vaporization wou¹ be equal to the rate of transfer of vapors from the pellet surface to the surrounding gas bulk. If k_{H_2} is the mass transfer coefficient for galena vapor to the bulk of surrounding hydrogen gas, rate of mass transfer would be given by

$$W_{H_2} = \frac{k_{H_2} . A . Pce}{RT} \qquad ...(5.2)$$

where Pce is the partial pressure of galena at the surface of the particle which is assumed to be equal to the equilibrium partial pressure, A is the surface area of the particle and R is the universal gas constant. For the sake of simplicity, the pellet was assumed to be a sphere of diameter d whose surface area was equivalent to that of the cylindrical pellet. It was further assumed that the effect of porosity of the pellet could be quantified using an emperical parameter ϵ such that

$$W_{H_2} = \frac{k_{H_2} . \pi d^2 . \epsilon Pce}{RT} \qquad ...(5.3)$$

There are however two unknown parameters (k_{H_2} and ϵ) in the above equation. The mass transfer coefficient k_{H_2} could be estimated using the Ranz-Marshall's correlation[39]

$$Sh = 2 + 0.6 \, (Re)^{1/2} \, (Sc)^{1/3} \quad \quad \ldots (5.4)$$

where   Sh is Scherwood's no. ($\frac{kd}{D}$)

    Re is Reynold's no. ($\frac{\rho vd}{\mu}$)

and   Sc Schmidt's no. $= \frac{\mu}{\rho D}$

ρ = density of the gas, μ is viscosity, D is binary diffusivity, d is the diameter of the sphere and v is the velocity of gas flow.

To estimate ϵ , the vaporization data of galena in nitrogen was used. It was assumed that ϵ depended only on the physical structur' of the pellet and therefore, as long as the physical structure remains constant ϵ will also be remained constant and that it is independent of the surrounding gaseous medium.

For nitrogen the rate of mass transfer will be

$$W_{N_2} = \frac{k_{N_2} \, \pi \, d^2 \, Pce}{RT} \quad \quad \ldots (5.5)$$

where W_{N_2} is the experimentally measured rates, (Table 5.4).
It would be possible to estimate ϵ using Equn. (5.5) . These
values were estimated for different R values and temperatures
and are tabulated in Table (5.5) . The values of mass
transfer coefficients K_{N_2} and K_{H_2} obtained using Equn (5.4) under
various experimental conditions are given in Table (5.6). Using
these values it was possible to estimate the vaporization
rates of galena in hydrogen. The estimated values are reported
in Table (5.5).

TABLE -5.4

Observed mass transfer rate of galena under various experimental conditions.

Temp. °C	Flow c.c/min.	W_{N_2}/moles/sec.			
		R=0	R=1	R=2	R=4
650	200	1.394×10^{-7}	2.755×10^{-7}	8.498×10^{-8}	4.012×10^{-8}
	400	1.580×10^{-7}	3.282×10^{-7}	1.204×10^{-7}	4.966×10^{-8}
	600	1.761×10^{-7}	3.575×10^{-7}	1.314×10^{-7}	5.759×10^{-8}
700	200	3.669×10^{-7}	3.436×10^{-7}	2.454×10^{-7}	6.515×10^{-8}
	400	6.198×10^{-7}	4.017×10^{-7}	2.643×10^{-7}	6.978×10^{-8}
	600	6.387×10^{-7}	4.600×10^{-7}	2.743×10^{-7}	7.799×10^{-8}
750	200	3.890×10^{-7}	1.002×10^{-6}	5.844×10^{-7}	2.532×10^{-7}
	400	4.635×10^{-7}	1.122×10^{-6}	7.055×10^{-7}	3.037×10^{-7}
	600	4.607×10^{-7}	1.188×10^{-6}	8.023×10^{-7}	2.902×10^{-7}
800	200	1.552×10^{-6}	1.940×10^{-6}	1.004×10^{-6}	4.559×10^{-7}
	400	1.415×10^{-6}	2.231×10^{-6}	9.161×10^{-7}	5.278×10^{-7}
	600	4.898×10^{-6}	2.493×10^{-6}	1.076×10^{-6}	5.679×10^{-7}

TABLE-5.5   62

Observed mass transfer rate of galena and ϵ under various experimental conditions.

Temperature °C	Composition	W_{H_2} moles/sec.	ϵ
	R=0	6.103×10^{-7}	396.2
650	R=1	1.190×10^{-6}	584.06
	R=2	2.088×10^{-7}	96.88
	R=4	1.726×10^{-7}	73.57
	R=0	1.61×10^{-6}	200.15
700	R=1	1.488×10^{-6}	139.71
	R=2	1.061×10^{-6}	94.22
	R=4	2.806×10^{-7}	22.96
750	R=0	1.73×10^{-6}	48.54
	R=2	2.56×10^{-6}	51.397
800	R=0	6.87×10^{-6}	50.73
	R=1	6.74×10^{-6}	37.63

TABLE -5.6

Calculated mass transfer co-efficient for hydrogen (k_{H_2}) and nitrogen (k_{N_2}) for different temperatures and compositions.

Temperature °C	Composition	k_{H_2}	k_{N_2}
	R=0	3.3611	0.7676
650	R=1	2.5892	0.5993
	R=2	2.4577	0.5705
	R=4	2.2784	0.5311
	R=0	3.6916	0.8404
	R=1	2.0425	0.6555
700	R=2	2.6980	0.6238
	R=4	2.501	0.5807
	R=0	4.0336	0.9071
	R=1	3.1050	0.7070
750	R=2	2.9466	0.6728
	R=4	2.7312	0.6261
	R=0	4.3580	0.9845
	R=1	3.354	0.7667
800	R=2	3.1825	0.7295
	R=4	2.949	0.6787

For k_{H_2} H_2 flow rate = 150 c.c/min.

For k_{N_2}, N_2 flow rate = 200 c.c/min.

CHAPTER -6

CONCLUSIONS

Vaporization

1. The amount of galena evaporated, increased with increase of temperature.

2. As vaporization involved mass transfer through the boundary layer, increase in gass flow rate resulted in higher weight loss due to fall in boundary layer resistance with higher flow rate.

3. Addition of lime resulted in increase of porosity and galena particles got dispersed, which prevented sintering of galena particle. This gave rise to higher weight loss due to vaporization with increase of lime content.

4. Plots of log $K_{v}, \dot{N}_2$ vs $1/T$ to calculate activation energy, parallel charascteristics at any flow rate with different lime content, indicating that addition of lime did not change the basic mechanism of vaporization.

Reduction

1. The extent of reduction was higher at higher flow rate of reducing gas at a given temperature for the same composition of the galena lime samples. It was due to fall in boundary layer resistance with increase in flow rate.

2. Reduction increased with increase in temperature upto $750^{o}C$ but at $800^{o}C$ it decreased. It is attributed to the sintering of galena particles at higher temperatures. Formation of some less voletile complex compound may also contribute to reduction in total weight loss at higher temperature. But this could not be verified.

3. Lime acted as a scavanging reagent and enhanced the rate of reduction of galena.

APPENDIX – I

VAPORIZATION DATA AT 650°C FOR VARIOUS COMPOSITIONS AND NITROGEN FLOW RATES.

Flow Rate (c.c./min)	Time (min)	% Wt.Loss			
		R=0	R=1	R=2	R=4
	5	3.16	3.46	3.53	4.14
	15	4.34	4.23	4.14	6.72
200	30	4.44	4.57	4.84	7.76
	45	4.62	5.21	5.60	8.78
	60	4.67	5.90	6.36	9.63
	5	3.83	3.39	3.73	5.85
	15	4.29	4.12	4.74	6.94
400	30	4.52	4.86	5.59	8.16
	45	4.62	5.82	6.60	9.36
	60	4.69	6.53	7.51	10.35
	5	3.77	3.68	3.75	6.28
	15	4.21	4.24	4.47	7.10
600	30	4.43	5.10	5.72	8.60
	45	4,53	6.09	6.85	9.88
	60	4.55	6.93	8.01	11.09

Contd.. APPENDIX –I

VAPORIZATION DATA AT 700°C FOR VARIOUS COMPOSITIONS
AN. NITROGEN FLOW RATES.

Flow Rate (c.c./min)	Time (min)	% Wt. Loss			
		R=0	R=1	R=2	R=4
	5	3.91	3.43	3.45	3.79
	15	4.05	3.92	4.17	4.77
200	30	4.37	5.51	5.12	6.19
	45	4.63	6.98	6.88	7.39
	60	4.78	8.20	8.18	8.52
	5	4.06	3.71	3.53	3.83
	15	4.29	4.11	4.80	4.84
400	30	4.45	5.67	5.94	6.23
	45	4.68	7.13	7.14	7.54
	60	4.85	8.46	8.30	8.84
	5	4.08	4.08	4.07	3.97
	15	4.85	4.92	5.05	5.75
600	30	5.50	6.36	6.67	6.84
	45	5.61	8.74	7.97	8.84
	60	5.73	9.63	9.28	10.23

Contd... APPENDIX-I

VAPORIZATION DATA AT 750°C FOR VARIOUS COMPOSITIONS
AND NITROGEN FLOW RATES.

Flow Rate (c.c/min)	Time (min)	% Wt. Loss			
		R=0	R=1	R=2	R=4
	5	3.92	3.93	5.09	5.94
	15	4.13	6.66	9.30	10.64
200	30	4.24	10.14	14.51	16.51
	45	4.36	12.82	18.82	21.28
	60	4.56	13.03	22.15	25.34
	5	4.07	4.11	6.20	6.52
	15	4.40	8.03	11.83	12.42
400	30	4.93	12.16	18.07	17.89
	45	5.07	15.06	22.38	24.10
	60	5.35	16.99	25.18	27.66
	5	4.72	4.63	7.58	10.04
	15	4.97	8.75	13.95	15.13
600	30	5.19	13.24	20.82	21.60
	45	5.44	16.40	25.31	26.19
	60	5.57	18.67	28.31	29.11

Contd... APPENDIX-I

VAPORIZATION DATA AT 800°C FOR VARIOUS COMPOSITIONS
AND NITROGEN FLOW RATES.

Flow Rate (c.c/min)	Time (min)	%Wt. Loss			
		R=0	R=1	R=2	R=4
	5	3.81	5.65	7.78	7.67
	15	4.17	11.84	15.88	17.46
200	30	4.34	17.55	23.55	26.38
	45	5.17	20.69	27.25	31.06
	60	5.63	22.49	27.89	32.08
	5	3.86	5.83	8.89	9.52
	15	4.53	12.48	17.81	19.60
400	30	4.98	18.58	24.89	28.74
	45	5.36	21.73	27.28	31.54
	60	5.74	22.56	27.93	32.30
	5	4.23	6.84	9.47	10.51
	15	4.64	14.29	18.87	20.81
600	30	5.07	20.07	26.02	29.04
	45	5.78	22.37	28.15	31.91
	60	6.52	25.11	28.93	32.53

APPENDIX −2

WEIGHT LOSS DATA FOR REDUCTION UNDER VARIOUS EXPERIMENTAL CONDITIONS

Temperature °C	Flow rate c.c/min	Time min.	% Wt loss				
			R=0	P=1	R=2	R=4	R=3
		5	0.02	0.02	0.2	0.6	
		15	2.06	2.60	2.76	3.49	
	150	30	4.02	5.23	6.11	6.53	
		45	5.23	6.83	7.65	9.12	
		60	5.78	7.96	8.70	11.33	
650		5	2.14	2.36	2.65	2.61	
		15	5.18	5.27	7.29	7.39	
	300	30	6.99	7.80	13.80	14.75	
		45	7.46	9. 2	18.5	19.87	
		60	9.23	11.40	20.85	21.45	
		5	0.04	0.05	2.61		3.07
		15	2.76	3.21	5.46		6.93
	150	30	4.36	6.55	10.11		10.92
		45	5.37	7.73	11.85		12.58
		60	5.89	10.43	12.39		12.95
700		5	1.58	3.12	3.62		3.79
		15	5.48	7.26	10.29		10.5
	300	30	7.29	12.92	15.87		19.97
		45	8.22	14.21	19.23		22.23
		60	9.35	15.67	21.27		22.23

Contd... APPENDIX

WEIGHT LOSS DATA FOR REDUCTION UNDER VARIOUS EXPERIMENTAL CONDITIONS.

Temperature °C	Flow rate c.c/min	Time min.	% Wt loss		
			R=0	R=1	R=2
750	150	5	0.6		3.01
		15	3.5		6.00
		30	5.1		10.8
		45	5.79		12.37
		60	6.34		14.2
	300	5	3.3		6.3
		15	5.67		11.42
		30	7.82		16.1
		45	8.99		19.74
		60	).98		21.93
800	150	5	0.3	1.15	
		15	2.52	4.73	
		30	3.47	6.21	
		45	4.92	8.25	
		60	5.21	11.63	

APPENDIX -3

DETERMINATION OF POROSITY

Porosity of a compact is defined as the ratio between volume of the pores and the volume of the compact. Mathematically it can be expressed as

$$\text{Porosity} = 1 - \frac{\text{Apparent density of compact}}{\text{True density of the powder}}$$

The apparent density of the compact was determined by weighing the specimen and volume of the pellet from its average length.

True density of the powder was determined by using a specific gravity bottle. Water was used as a liquid of known density. The following procedure was adopted for determining the true density.

Weight of the bottle $= W_b$

Weight of the bottle + sample $= W_1$

Weight of the bottle + sample + water $= W_2$

Weight of the bottle + water $= W_3$

Density of water at $30^\circ C$ $= 0.9956$ gm/c.c.

Density of the powder $= \dfrac{W_1 - W_b}{(W_3 - W_b) - (W_2 - W_b)} \times 0.9956.$

APPENDIX −4

ATTEMPTS TO ESTIMATE METALLIC LEAD IN REDUCED SAMPLE

Various attempts were made to analyse the
amount of metallization of galena after reduction under
different experimental conditions. Some of them are described
below

(a) Leaching and Melting:− Lead being a low melting point
element ($327^{\circ}C$), it was expected that lead might come out in
the form of droplet when heated to a relatively high temper-
ature. The presence of lime, CaS, iron compound and zinc
compound might effect the droplet formation of lead . So
the reduced samples were first powdered and then leached with
10% HCl. The filtrate was tested chemically to confirm the
presence of Ca, Fe, Zn ions. Some leaching experiments with
10% HCl was carried out with Pb, Pb+PbS, Pb+PbS+CaO mixtures
to have quantitative idea about the dissolution characteristics
of Pb, PbS and CaO. It was found that around 5% Pb, 22−25% PbS
and almost 100% CaO got dissolved in 10% HCl.

The residue of the reduced sample after leaching over
the filter paper was then dried up and was carefully transferred
to a 1.27 cm diameter and 4 cm long quartz tube. The tube

containing the residue was evacuated to 10^{-4} atmosphere pressure and sealed. The idea of evacuation was to confirm that lead, that was formed, should not get oxidized by reacting with O_2 of air. This evacuated capsule was heated at a temperature of $700^{\circ}C$.

Unfortunately most of the capsules got burst inside the furnace during heating. It may be due to increase of gas pressure of some unidentified species.

Another attempt, made to seperate out the formed lead, mixed with unreacted galena, was by heating the leached residue in nitrogen and slightly reducing atmosphere at a temperature of $700^{\circ}C$ by taking the sample in crucible. But this experiment came out with no positive result.

(b) X- ray Analysis of the Reduced Sample:- To study the reaction mode during reduction of samples with and without lime, powder of reduced samples were analysed by X- ray diffraction method. It was found that for sample where no lime was used contain lead and galena after reduction whereas sample where lime was used confirmed the presence of calcium sulfide, calcium oxide, lead and galena. This shows that when no lime was used the reduction took place in direct manner as indicated in Reaction 5a and in presence of lime, the scavenged reaction took place according to the Reaction 5b.

The X- ray analysis data for two samples are presented in
Appendix 5 .

(c)   Estimation of Residual Sulfur:-   In the partially
reduced sample a part of the galena remained unreacted.
So if the amount of sulfur present in the sample after
reduction could be estimated, % desulfurization could easily
be calculated from the initial sulfur content of galena. Thus
an affort was made to liberate the sulfur from the sample by
reacting with HCl according to the following reaction

$$PbS + 2HCl = PbCl_2 + H_2S$$
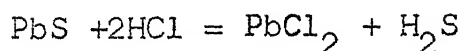
and liberated H_2S was tried to be precipitated as a sulfide
compound like CdS by reacting with $CdCl_2$ solution. But it was
found that the dissolution of galena in HCl was incomplete and
the liberation of H_2S w $\jmath$ partial.

APPENDIX −5

RESULT OF X−RAY ANALYSIS

SAMPLE: REDUCED PELLET WITHOUT LIME AT TEMPERATURE 700°C
AND HYDROGEN FLOW RATE 300 c.c./min.(COPPER TARGET)

2θ	Intensity	d	Standard Value	Phase
26.0	84*	3.4241*	3.429*	PbS
28.55		3.1238		
30.1	100*	2.9664*	2.969*	PbS
31.3	100	2.8553	2.855	Pb
32.3		2.7692		
35.8		2.5060		
36.3	50	2.475		Pb
39.8		2.2629		
43.1	57*	2.0998*	2.099*	PbS
47.8		1.9012		
51.1	35*	1.7859*	1.790*	PbS
52.3	31	1.7477	1.75	Pb
53.4	16*	1.7128*	1.714*	PbS
56.35		1.6313		
62.6	10*	1.4826*	1.484*	PbS

* Represent values for galena.

SAMPLE: RESUCED PELLET WITH R=1 AT TEMPERATURE $650^{o}C$
AND HYDROGEN FLOW RATE 300 c.c/min. (COPPER
TARGET).

2θ	Intensity	d	Standred Value	Phase
26.05	84*	3.4176*	3.429*	PbS
27.1		3.2875		
28.08		3.1750		
30.1	100*	2.9664*	2.969*	PbS
31.3	100	2.8553	2.855	Pb
31.5	100°	2.837^{o}	2.846^{o}	CaS
32.3	34^{X}	2.769^{X}	2.778^{X}	CaO
36.35	50	2.4694	2.475	Pb
37.3	100	2.4047^{X}	2.405^{X}	CaO
43.08	57*	2.0979*	2.099*	PbS
44.6	70°	2.0299^{o}	2.013^{o}	CaS
47.55		1.9106		
51.0	35*	1.7892*	1.790*	PbS
52.3	31	1.748	1.750	Pb
53.4	16*	1.7143*	1.714*	PbS
53.7	45^{X}	1.705^{X}	1.701^{X}	CaO
6i.44		1.5078		
62.15	32	1.4923	1.493	Pb
62.49	10*	1.4850*	1.4826*	PbS

2θ	Intensity	d	Standred Value	Phase
63		1.4742		
64.3	10 [X]	1.447 [X]	1.451 [X]	CaO
65.5	10 [O]	1.4232 [O]	1.4238 [O]	CaS

*-Represent values for galena

x-Represent values for calcium oxide

o-Represent values for calcium sulfide.

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